

Research Article

Square Wave Voltammetric Determination of Residues of Carbendazim Using a Fullerene/Multiwalled Carbon Nanotubes/Nafion[®]/Coated Glassy Carbon Electrode

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A glassy carbon electrode (GCE) was modified with a fullerene/Multiwalled Carbon Nanotubes (MWCNTs)/Nafion composite and applied to the determination of carbendazim, a fungicide. The voltammetric behavior of the analyte was investigated using Cyclic Voltammetry (CV), on the bare GCE and on the same electrode coated by a thin film of the composite material. The electrode response was more than fourfold important on the modified electrode, due to electrical conductivity of fullerene and MWCNT and to favorable electrostatic interaction between the negatively charged Nafion and the protonated fungicide. A sensitive electroanalytical procedure based on Square Wave Voltammetry (SWV) was then developed to detect the analyte. Under the optimum conditions, a linear relationship was obtained between the peak current and the concentration of carbendazim, in the range from 2.0×10^{-8} mol/L to 3.5×10^{-7} mol/L, leading to a detection limit of 1.7×10^{-8} mol/L and to a quantification limit of 5.57×10^{-8} mol/L. The developed procedure was successfully applied to detect carbendazim upon adsorption by some ferritic soils.

1. Introduction

Carbendazim or methyl 1H-benzimidazole-2-ylcarbamate (MBC) is a fungicide that belongs to the benzimidazole group. When applied on soils, it persists for a long time, because its degradation is slow [1] and it is harmful to the human body. Several analytical methods have been proposed for the quantitative determination of this compound. These methods include high performance liquid chromatography, capillary electrophoresis, liquid chromatography/time-of-flight mass spectrometry, and ultraperformance liquid chromatography coupled to tandem mass spectrometry [2–10]. MWCNTs are now considered as important electrode modifiers due to their ability to promote electron transfer in electrochemical reactions and to their strong capability to contribute to the electrocatalytic effect [11]. Due to the electrochemical properties of fullerenes, their application as new and

effective electrocatalysts for various chemical and biochemical reactions and the designing of electrochemical sensors based on fullerenes are under increasing investigation [12].

Besides, Nafion is a perfluorinated sulfonated cation exchanger polymer that has been widely used in electrochemistry to modify electrodes because it possesses many excellent properties such as chemical inertness, thermal stability, mechanical strength, huge cation exchange capacity, and antifouling properties [13]. Therefore, it is expected that, by combining carbon nanotubes and fullerenes and Nafion as electrode modifier, a synergistic effect of these components could lead to a sensitive sensor. In this work, it is found that fullerene/MWCNT can be easily dispersed into ethanol in the presence of Nafion, giving a stable and homogeneous fullerene/MWCNT/Nafion dispersion. A sensor was thus developed, which results from the coating of a glassy carbon electrode using the previously mentioned dispersion. The

developed sensor was optimized and critically compared with a spectrophotometric method both used to quantify residues of MBC upon adsorption by soil samples.

2. Experimental

2.1. Apparatus and Reagents. Electrochemical measurements were carried out using a μ -Autolab potentiostat-galvanostat (type III) running with the GPES software, supplied by EcoChemie, Utrecht (Netherlands). A standard single compartment three-electrode cell was used. Electrode potentials were measured with respect to an Ag/AgCl/3 M KCl reference electrode (Metrohm, Ref 6.0726.100). A stainless steel rod was used as counter electrode. The working electrode was a fullerene/MWCNT/Nafion modified GCE prepared as described below.

Upon adsorption by soils, MBC concentration of the filtrates was spectrophotometrically determined using a JENWAY Spectrometer. IR spectra of soils samples were obtained at room temperature in the spectral range from 4500 to 375 cm^{-1} with a resolution of 2 cm^{-1} , on a Spectrometer (Alpha, Bruker Optics) equipped with the OPUS/Mentor software which provides an intuitive interface and facilitates the analysis of scans.

MBC (99%) was purchased from Riedel-de-Haën. Fullerene/MWCNT mixture powder (95%, 3–20 nm OD, 2–5 nm ID, 0.1–10 μm length) and Nafion (5% w/w in EtOH) were obtained from Alfa Aesar. NH_4Cl , H_3PO_4 ($\geq 85\%$), KH_2PO_4 , and K_2HPO_4 were obtained from Sigma-Aldrich. CH_3COOH , CH_3COONa , H_2SO_4 , $\text{CH}_3\text{CH}_2\text{OH}$, and all other chemicals were of analytical reagent grade and used as received. The solutions and subsequent dilutions were prepared with distilled water.

2.2. Electrode Surface Modification Procedure. Prior to its modification by drop-coating, each GCE was polished with alumina pastes of different sizes (1, then 0.05 μm) on billiard cloth. They were then placed in a 1:1 ethanol-water solution and properly cleaned in a sonicator for 10 min to eliminate any remaining alumina particles. 2 mg of fullerene/MWCNT was dispersed in 1 mL Nafion (5%) and then in 1 mL ethanol by ultrasonication for 1 hour to give homogeneous fullerene/MWCNT/Nafion and fullerene/MWCNT dispersions. The GCE surface was coated with 7 μL of each resulting dispersion and dried at room temperature for 30 min to obtain, respectively, fullerene/MWCNT/Nafion/GCE and fullerene/MWCNT/GCE that were afterwards used as working electrodes.

2.3. Electrochemical Procedure. All experiments were performed at room temperature. The electrochemical behavior of MBC was investigated using the bare and modified GCEs, by CV performed in the potential window of 0.4 to 1.5 V versus Ag/AgCl (at a scan rate of 100 mV/s). The stripping voltammetric determination of MBC was carried out by SWV following 2 steps: (i) the accumulation at open circuit of MBC at the working electrode immersed in 10 mL of acetate buffer solution (0.01 mol/L, pH 4) containing MBC and kept under stirring; (ii) the detection of accumulated MBC in

ammoniacal buffer (0.1 mol/L, pH 9) used as supporting electrolyte. An accumulation time of 8 min at open circuit was used for quantitative measurements. The scan parameters included a pulse potential frequency of 25 Hz, an amplitude of 80 mV, a scan rate of 250 mV/s, and a step potential of 10 mV. Following each measurement, the electrode was cleaned by stirring in distilled water until obtaining a flat voltammogram.

2.4. Soil Samples and Sorption Study. Two soil samples originating from Nkounke (Foumbot, West Region, Cameroon) were characterized and used in this study. They are NK1 collected between 20 and 33 cm in depth and NK3 sample collected on a savanna cultivated soil between 0 and 20 cm in depth. For the adsorption of MBC by soil samples, a given mass of soil was weighed and introduced into 25 mL flask containing 15 mL of a solution of a known concentration of MBC. Each flask was then hermetically closed, placed on an agitator, and agitated for 60 min. The mixture was allowed to rest for a few minutes, then a part of the solution from the upper liquid layer was removed using a micropipette, and the concentration of residual MBC was determined using both SWV and spectrophotometry.

3. Results and Discussion

3.1. Electrochemical Behavior of MBC on Fullerene/MWCNT/Nafion/GCE. The electrochemical behavior of 3×10^{-5} mol/L MBC on different electrodes was studied by CV in 0.01 mol/L acetate buffer at pH 5 and Figure 1 presents the obtained voltammograms: one can notice that the electrochemical behavior of MBC at all investigated working electrodes is a quasi-reversible oxidation [14, 19]. The electrochemical response at fullerene/MWCNT/Nafion/GCE was more pronounced in terms of peak current. This can be explained by the high electrical conductivity of fullerene/MWCNT and electrostatic interactions between the negatively charged Nafion (bearing SO_3^- groups) and the protonated amine groups (NH_3^+) of MBC [22]. This electrode was exploited for further experiments as working electrode.

3.2. Influence of Mass of Fullerene/MWCNT. The accumulation capacity of the thin film on the GCE is expected to depend on the amount of fullerene/MWCNT in the dispersion used to modify the electrode surface. The anodic peak intensity increases with an increase in the amount of fullerene/MWCNT and reaches a maximum value corresponding to 3 mg of fullerene/MWCNT (Figure 2(a)). Beyond this mass, current intensity decreases. This can be explained by the fact that the suspension becomes more consistent and thus forms a barrier to electron transfer. 3 mg is then taken as the optimal amount of fullerene/MWCNT in the dispersion.

3.3. Influence of Nafion Concentration. Keeping the amount of fullerene/MWCNT constant in the dispersion used to modify the GCE surface (3 mg in 1 mL EtOH), the amount of Nafion introduced in that dispersion was varied. Figure 2(b)

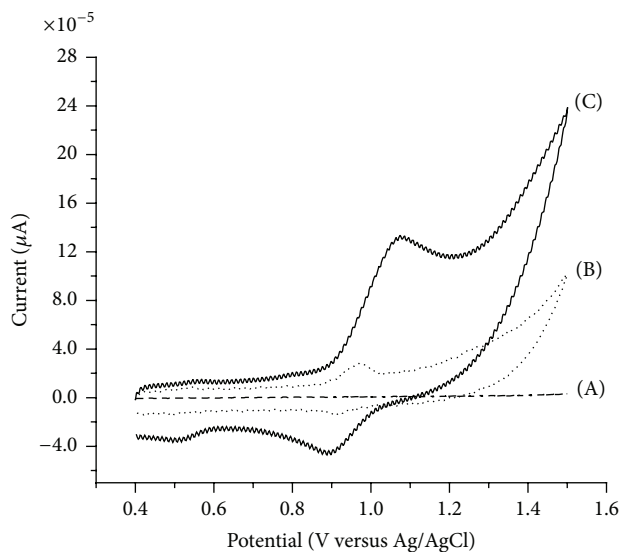


FIGURE 1: Cyclic voltammograms recorded in 0.01 mol/L acetate buffer (pH 5) for 3×10^{-5} mol/L MBC on (A) bare GCE, (B) fullerene/MWCNT/GCE, and (C) fullerene/MWCNT/Nafion/GCE. Potential scan rate: 100 mV/s.

presents the evolution of anodic peak current (I_p) versus the percentage of Nafion; I_p decreases with an increase in Nafion concentration. For dispersion containing 1 to 2%, the electrode response was relatively high and decreased as the dispersion became more concentrated as observed by de Oliveira et al. (2004) [22]. This feature could be due to a more viscous dispersion that limits the mass transfer of MBC within the bulk of working electrode. A dispersion containing 1% Nafion was taken as optimal concentration in the subsequent experiments.

3.4. Influence of pH of Detection and Accumulation Media. Figure 3(a) shows the variation of the electrochemical response in 0.1 mol/L ammoniacal buffer at different pH values, upon preconcentration in 0.01 mol/L acetate buffer solution (pH 5) containing 4×10^{-6} mol/L MBC. The detection of MBC was quite low in acidic medium, but favorable in basic medium, similarly to a previous published work (Hernandez et al., 1996) [14]. A 0.1 mol/L ammoniacal buffer solution at pH 9 was further selected as optimal detection medium. The variation of the accumulation medium pH (Figure 3(b)) shows that current intensities increase in acidic solution from pH 1 to pH 4 and then diminish steeply to pH 8. The maximum current is recorded when the accumulation is performed at pH 4, a value close to the pK_a of MBC (4.5) and to a value previously obtained by Ribeiro et al. (2011) [19]. This could be explained by the protonated form of MBC which is best accumulated for pH before its pK_a , due to the presence of the negatively charged Nafion at the composite material at the electrode.

3.5. Influence of Deposition Potential. Figure 4 shows the variation of peak current as a function of electrolysis potential. A maximum is reached at -0.4 V and the peak

current drops beyond this value which was taken as the best compromise for the electrolysis of MBC on the fullerene/MWCNT/Nafion/GCE working electrode.

3.6. Influence of Accumulation Time. The SWV peak current of MBC was highly dependent on preconcentration time, as shown on Figure 5. Between 60 and 300 s accumulation time, the electrode signal was almost linear, reaching a plateau when preconcentration was performed between 300 and 500 s. It appears that a saturation of exchange sites at the working electrode is reached after 300 s preconcentration. For subsequent analyses, the accumulation of MBC was performed for at least 8 min prior to its detection by SWV.

3.7. Stability and Reproducibility of Electrode. Reproducible current responses were noticed and the results from four different electrodes recorded by analyzing a solution of 5×10^{-7} mol/L MBC yielded a relative standard deviation (RSD) value of 3.12%. The stability of the response was measured with the same electrode after five measurements with 2×10^{-6} mol/L MBC, leading to a RSD value of 0.25%. This indicated that the developed method is reliable and reproducible.

3.8. Calibration Curve. Under the optimized conditions established in previous sections, the concentration of MBC was varied in the range of 2×10^{-8} mol/L to 3.5×10^{-7} mol/L and Figure 6(a) presents the curves obtained by SWV. A linear dependence was observed between the electrode response expressed as peak current (I_p) and MBC concentration, according to the equation I_p (A) = 420.97 [MBC] (mol/L) + 2.28141×10^{-6} characterized by a correlation coefficient (R^2) of 0.999 (Figure 6(b)). The limit of detection LOD ($3 SD/m$) is 1.7×10^{-8} mol/L and the limit of quantification LOQ ($10 SD/m$) is 5.57×10^{-8} mol/L, where SD is the blank standard deviation and m is the slope of the calibration curve [22, 23].

The performance of the fullerene/MWCNT/Nafion/GCE was compared to reported methods and modified electrodes for the determination of MBC, as shown in Table 1. It is observed that fullerene/MWCNT/Nafion/GCE exhibited a good LOD, a low peak potential, and a high sensitivity.

3.9. Interference Study and Analytical Application. The developed analytical method was applied to the quantification of MBC upon adsorption by 2 soil samples. Prior to that, the influence of some ions (likely to exist in soils such as K^+ , Na^+ , Ca^{2+} , Mg^{2+} , and Fe^{3+}) on the peak currents of MBC was studied using 6×10^{-8} mol/L MBC ($I_p = 2.53 \times 10^{-5}$ A) in the supporting electrolyte (Table 2). The results for three tests of each ion indicated that concentration 1000 times that of MBC did not significantly affect the determination of MBC.

The utility of the modified electrode prepared in this study for the determination of MBC was tested in a comparative way. Thus, two soils samples with characteristics gathered in Table 3 were used as sorbents to adsorb MBC. The FTIR spectra of NK1 and NK3 soil samples recorded in the 300–4000 cm^{-1} region are, respectively, presented in Figure 7.

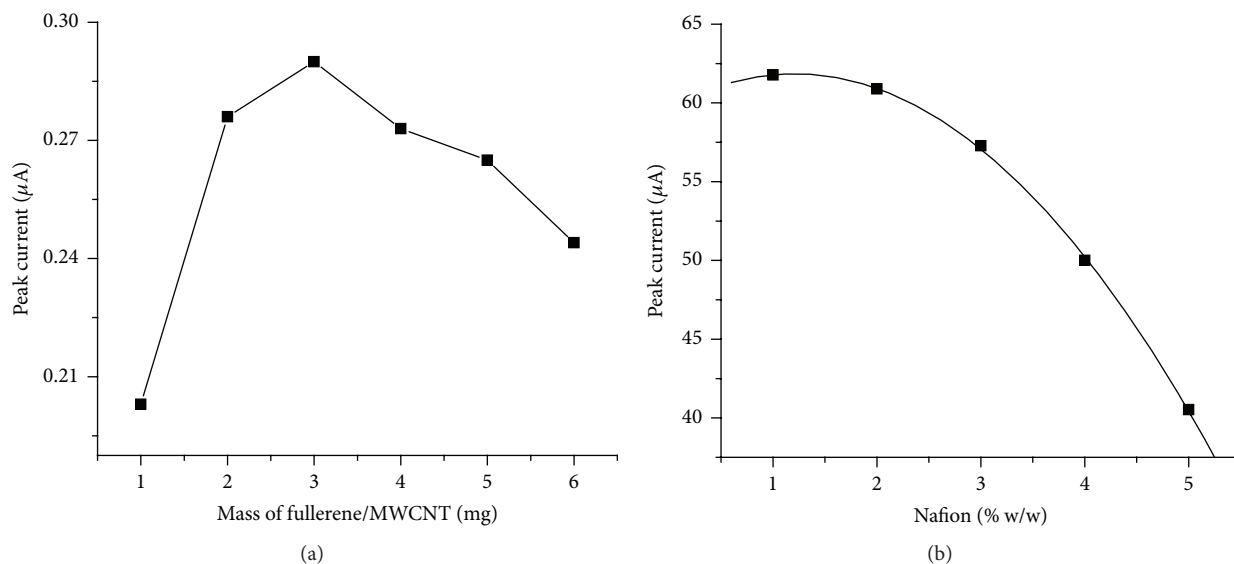


FIGURE 2: (a) Effect of the amount of fullerene/MWCNT (mg) in 2 mL of Nafion (5%) on the SWV peak current of 7.84×10^{-6} mol/L MBC. (b) Effect of Nafion concentration on the peak current of 10^{-5} mol/L MBC. Experimental conditions: accumulation in 0.01 mol/L acetate buffer (pH 5); stripping analysis after 60 s deposition at -0.6 V, scan rate: 250 mV/s, amplitude: 0.02 V, and frequency: 25 Hz.

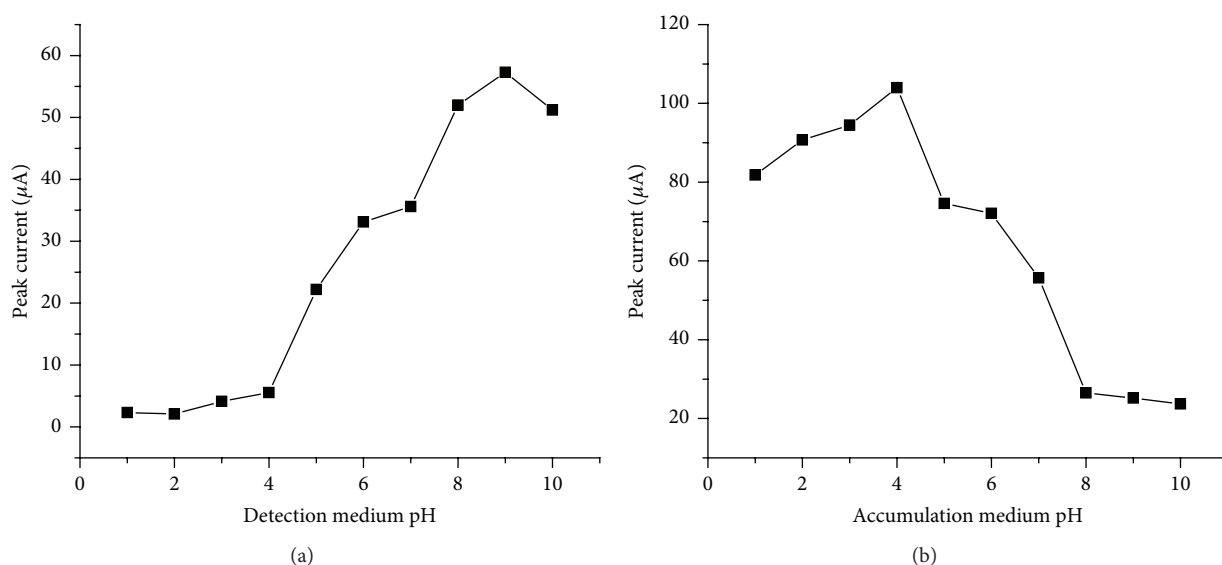


FIGURE 3: (a) Effect of detection medium pH on the peak current of 4×10^{-6} mol/L MBC. (b) Effect of pH of accumulation medium on the electrode response. For both curves, preconcentration was performed for 10 min in 0.01 mol/L acetate buffer (pH 5) containing 4×10^{-6} mol/L MBC, while detection was performed in 0.1 mol/L ammoniacal buffer (pH 9). Other experimental conditions as in Figure 2.

The absorption bands at 3690 and 3625 cm^{-1} in NK3 sample and 3694 and 3619 cm^{-1} in NK1 sample correspond to interlayer hydroxyl group stretching of kaolinite in samples [24, 25]. The absorption bands observed around 1400 and 1630 cm^{-1} in Figure 7 are ascribed, respectively, to C-H stretching vibration of organic matter and O-H deformation of molecular water [26, 27], while the bands around 1000 and 910 cm^{-1} could be ascribed, respectively, to Si-O and Al-OH stretching vibration bands of kaolinite. Also, the

band observed at $745\text{--}790\text{ cm}^{-1}$ can be ascribed to Si-O-Si intertetrahedral bridging bonds in silica contained in kaolinite as major mineral [25].

For sorption experiments, a known volume of 5×10^{-5} mol/L MBC was added to each soil sample and after 60 min agitation, the amount of MBC in the residual solution was determined as described in the experimental section.

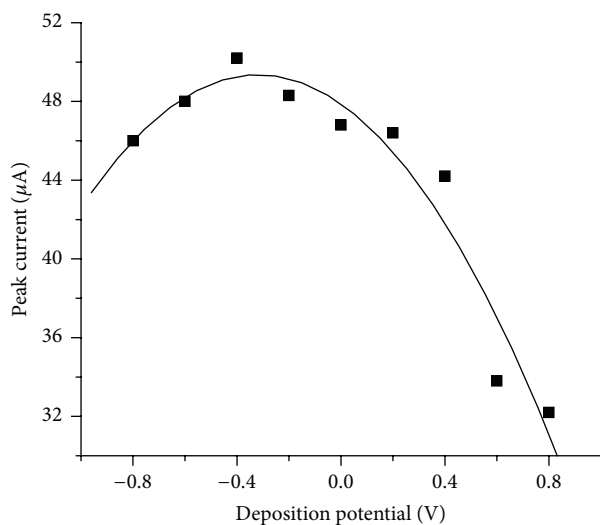
Table 4 compares the results obtained by the developed electrochemical method and by UV-Visible spectroscopy. For

TABLE 1: Comparisons of different modified electrodes used to assess the MBC amperometric response.

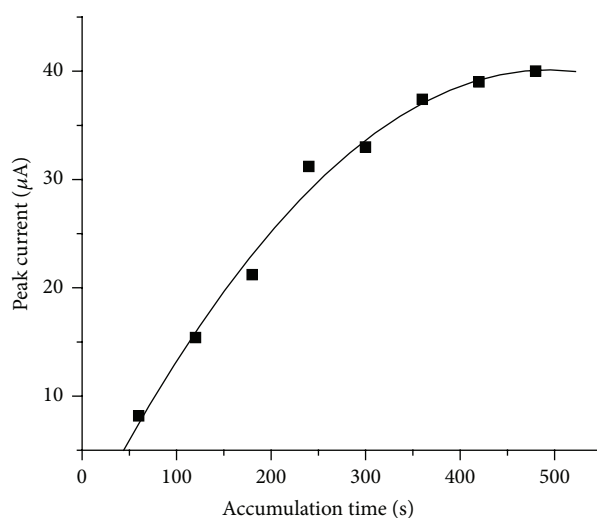
Modified electrode	LOD (mol/L)	Sensitivity (A mol ⁻¹ L)	Potential (V)	Reference
Silicone OV-17/GCE	4.8×10^{-8}	2.868	—	[14]
MC/GCE	9.6×10^{-7}	0.0896	1.5	[15]
MWNTs/GCE	5.2×10^{-8}	0.01861	1.4	[16]
MWNT-PMRE/GCE	9.0×10^{-9}	2.31	1.22	[17]
CD-GNs/GCE	2.0×10^{-9}	301.02	0.78	[18]
MWCNT/GCE	5.5×10^{-8}	4.28	0.96	[19]
GO-MWCNT/GCE	5.0×10^{-9}	2.73	1.1	[20]
SiO ₂ /MWCNT/GCE	5.6×10^{-8}	0.485	0.73	[21]
Fullerene/MWCNT/Nafion/GCE	1.7×10^{-8}	419.69	0.67	Present work

TABLE 2: Influence of ionic species on the peak current of 6×10^{-8} mol/L MBC ($I_p = 2.53 \times 10^{-5}$ A) in 0.1 mol/L ammoniacal buffer at pH 9.

Ionic species	Concentration (mol/L)	Contribution (%) $*I_{p[MBC]} = 100\%$
Ca ²⁺	6×10^{-5}	-1.42
Mg ²⁺	6×10^{-5}	+1.84
K ⁺	6×10^{-5}	-1.78
Na ⁺	6×10^{-5}	-1.90
Fe ³⁺	6×10^{-5}	-1.84

* $n = 3$.FIGURE 4: Effect of deposition potential on the peak current of 10^{-6} mol/L MBC, after 10 min preconcentration in 0.01 mol/L acetate buffer (pH 5) and detection in 0.1 mol/L ammoniacal buffer (pH 9). Other experimental conditions as in Figure 2.

the determination using SWV, 100 μ L of residual solution was added to 50 mL of the supporting electrolyte. After three replicate measurements, the mean generated currents were 1.818×10^{-5} A and 1.841×10^{-5} A, respectively, for NK1 and NK3 samples. The corresponding concentrations were calculated using the equation of the calibration curve. Finally,

FIGURE 5: Effect of accumulation time on peak current of 1.2×10^{-7} mol/L MBC in 0.1 mol/L ammoniacal buffer at pH 9. Other SWV experimental conditions: amplitude: 0.08 V, deposition potential: -0.4 V, and frequency: 25 Hz.

the concentration of MBC in the filtrate was calculated using the dilution effect. By UV-Vis spectroscopy (Table 4), the absorbance of the filtrate was measured (NK1: 0.101, NK3: 0.119) and the corresponding concentrations of the filtrate were calculated using its equation calibration ($Y = 14990.90909X - 0.1332$). From Table 4, both soils adsorb each more than 60% of the amount of the MBC initially present. However, one can notice that the recovery rate for the voltammetric method is higher than that obtained with spectrophotometric method. This reveals that the sensor herein proposed can be favorably exploited in soil sciences for the analysis of MBC.

4. Conclusion

This work has developed a composite fullerene/MWCNT/Nafion based sensor to detect carbendazim residues. Under the selected conditions, the oxidation peak current was proportional to MBC concentration in the range of

TABLE 3: Physicochemical characteristics of the studied soils.

Sample code	Depth (cm)	pH KCl	pH H ₂ O	Δ pH	CEC (meq/100 g)	Exchangeable acidity (meq/100 g)	OC (%)	OM (%)	Humidity (%)	Clay (%)	Silt (%)	Sand (%)
NK1	20-33	4.69	6.38	1.69	21.68	1.18	2.64	4.60	2.01	31	27	42
NK3	0-20	4.02	5.52	1.50	24.32	3.58	2.94	5.07	0.70	35	25	40

CEC (meq/100 g): cation exchange capacity; OC: organic carbon; OM: organic material.

TABLE 4: Residual concentration of MBC determined by spectroscopy UV-Visible and square wave voltammetry measurements.

Soil samples	[MBC] added (mol/L)	UV-VIS Spectroscopy measurement				Square wave voltammetry measurement			
		Absorbance measured*	RSD (%)	[MBC] found (mol/L)	Recovery (%)	Intensity* measured (A)	RSD (%)	[MBC] found (mol/L)	Recovery (%)
NK1	5×10^{-5}	0.101	2.6	1.56×10^{-5}	31.2	1.818×10^{-5}	1.8	1.89×10^{-5}	37.8
NK3	5×10^{-5}	0.119	1.9	1.60×10^{-5}	32.0	1.841×10^{-5}	1.0	1.92×10^{-5}	38.4

*n = 3.

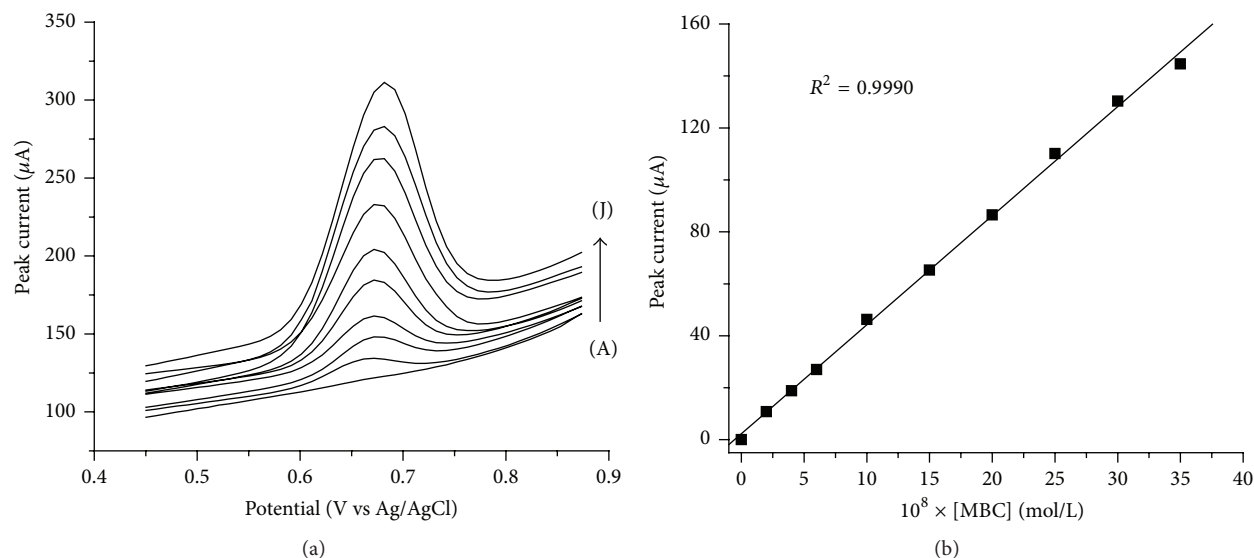


FIGURE 6: (a) SWV voltammograms of MBC at fullerene/MWCNT/Nafion/GCE obtained under optimized conditions, for MBC concentration from (A) to (J): 0, 2, 4, 6, 10, 15, 20, 25, 30, and 35×10^{-8} mol/L. (b) Calibration curve of MBC.

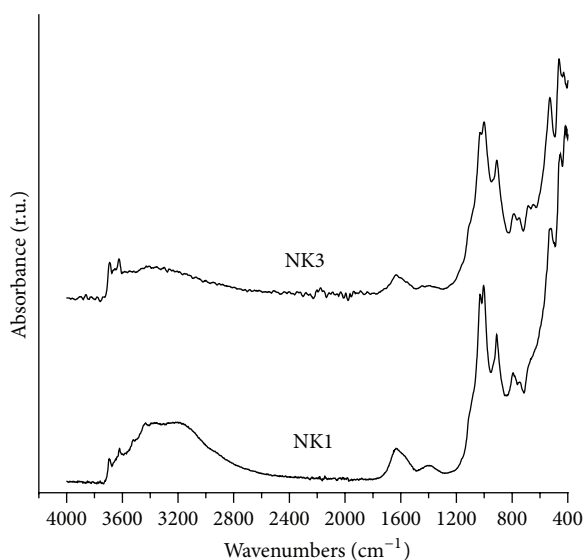


FIGURE 7: IR spectra ($4000\text{--}400\text{ cm}^{-1}$) NK1 and NK3 soil samples.

2.0×10^{-8} mol/L to 3.5×10^{-7} mol/L, and a novel voltammetric method for the determination of MBC was developed with the detection limit as low as 1.7×10^{-8} mol/L. The proposed method, shown to be reliable, was further applied to detect MBC upon adsorption by soil samples.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

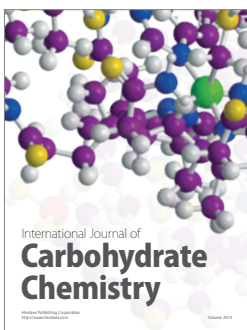
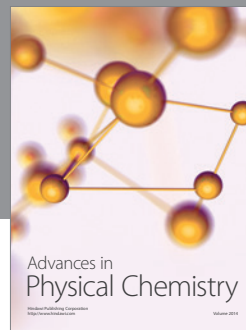
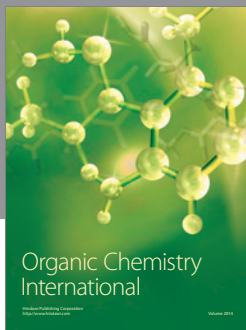
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